



## **Analysis of Commercially Available Zinc Phosphide from Bangladesh — Implications for Rodent Control**

Richard L. Bruggers,<sup>a\*</sup> Doreen L. Griffin<sup>a</sup> & M. Emdadul Haque<sup>b</sup>

<sup>a</sup>USDA/APHIS/ADC Denver Wildlife Research Center, P.O. Box 25266, Denver, CO  
80225-0266, USA

<sup>b</sup>Bangladesh Agricultural Research Institute, Vertebrate Pest Section, Joydebpur, Gazipur  
1701, Bangladesh

### **ABSTRACT**

*Farmers in Bangladesh seem reluctant to purchase zinc phosphide ( $Zn_3P_2$ ) for use in rodent control, primarily because of a concern over the quality of the technical powder available from local distributors. During 1988, packets of  $Zn_3P_2$  were purchased from the shelves of 23 distributors in Bangladesh and analyzed for technical purity. Only 2 of 23 distributors sold  $Zn_3P_2$  containing at least 80% (a.i.), while 14 distributors sold material ranging from 15% to nondetectable. Such a lack of quality control is not acceptable if farmers in Bangladesh are to use this material as a primary method of rodent control in agriculture.*

### **INTRODUCTION**

The acute rodenticide,  $Zn_3P_2$ , is used worldwide for controlling urban and field rodents (Hood, 1972; Tongtavee, 1978; Lund, 1988). Barnett & Prakash (1975) reported that at concentrations of 1–5% it would control rodents such as the lesser bandicoot rat (*Bandicota bengalensis*). Field crops such as rice and wheat in Bangladesh can receive significant preharvest damage from the bandicoot rat and other rodent species. Poché

\*To whom correspondence should be addressed.

*et al.* (1982) reported 12.1% losses to standing wheat, Ahmed *et al.* (1986) reported 5.7% losses to deepwater rice, and Sultana & Jaeger (1992) described wheat and rice losses as 2.3 and 1.9% of the expected yields in two areas of Bangladesh between 1986 and 1988, respectively. Such losses are considerable in a country like Bangladesh, and simple, inexpensive methods and clearly defined control strategies to reduce these losses are needed.

A number of rodenticides and baits were tested in crops in Bangladesh in the late 1970s and early 1980s (Poché *et al.*, 1979). One method that proved effective was placing 2%  $\text{Zn}_3\text{P}_2$  bait cakes in bandicoot rat burrow systems in crop fields (Brooks & Siddique, 1982). This technique was a slight modification of one first used in Pakistan by Smythe & Khan (1980) with baits consisting of 3.0% (not 2%)  $\text{Zn}_3\text{P}_2$  (80% a.i.), 2.0% oil, and a bait base of 47.5% of broken rice or wheat and 47.5% flours. This material was mixed with water into a paste, cut into  $2 \times 2$ -cm blocks, and air-dried. With the development of this technology, large-scale field demonstrations in Bangladesh were possible. In 1983 and 1984, these baits were prepared and provided to farmers in effective rodent control campaigns (Adhikarya & Posamentier, 1987). After a 1-year hiatus, annual rodent control campaigns were reinitiated. However, in the late 1980s, fewer farmers seemed to practice rodent control, apparently due to lack of an effective rodenticide, lack of a clearly defined control strategy, and/or lack of a way to assure cooperative and synchronized control among neighbors (Sultana & Jaeger, 1992). Farmers had increasingly lost confidence in the quality of the technical powder they purchased from local shops. Our research, conducted to determine the quality of the  $\text{Zn}_3\text{P}_2$  available to farmers, documents the lack of quality control for this material among commercial distributors.

## METHODS

From one to five packets of  $\text{Zn}_3\text{P}_2$  powder were purchased from 23 different commercial distributors in Dhaka, Comilla and Mirzapur during June and July, 1988. Five additional packets were purchased from nine of these same distributors in June 1989, and four more packets were purchased from two of the original distributors in July 1989 to compare purity over time. Normally, farmers purchase these packets to mix with grain. Although most packets were not labeled with content, we were usually told that the powder was 80%  $\text{Zn}_3\text{P}_2$  (the concentration of the import product). Although most farmers have little understanding of the importance of this percentage relative to their preparation of baits,

farmers expect the powder they purchase to be sufficiently pure to kill rats. The material in the packets was weighed, resealed in glass vials or plastic tubes, and sent to the USDA/APHIS/ADC Denver Wildlife Research Center (DWRC) for technical assay. Upon arrival, samples were logged in and maintained at ambient temperature until analysis. The 1988 samples were analyzed in May 1989, and the June/July 1989 samples were analyzed in July/August, 1989. A sample of material from each packet was assayed using DWRC Analytical Method 11A (USDA/APHIS/ADC — DWRC, 1989). In addition, material from each packet obtained from one distributor (DFN) was analyzed twice to assess method reproducibility.

The chromatographic method entailed measuring the phosphine gas that was liberated during sulfuric acid hydrolysis of  $\text{Zn}_3\text{P}_2$ . Ten milligrammes of material was placed in a 1 L Erlenmeyer flask. Sulfuric acid (40 ml of 10% v/v) was then added to the flask, which was quickly capped with a rubber septum. The flask was then allowed to equilibrate for 3 h with intermittent stirring to allow the  $\text{Zn}_3\text{P}_2$  to completely hydrolyze. The chromatographic system consisted of a Hewlett-Packard (Avondale, PA) 5880 gas chromatograph equipped with a flame photometric detector (FPD) operating in the phosphorous mode. A 30 m  $\times$  0.53 mm i.d. GS-Q capillary column (J&W Scientific, Folsom, CA) was used with a helium carrier ( $5.5 \text{ ml min}^{-1}$ ). The injection port temperature was  $70^\circ\text{C}$ , the detector temperature was  $190^\circ\text{C}$ , and the oven was maintained isothermally at  $60^\circ\text{C}$ . The flasks were sampled through the septum with a  $10 \mu\text{l}$  gastight syringe, and  $5 \mu\text{l}$  splitless injections were made (using a split vent flow of  $20 \text{ ml min}^{-1}$  and a purge time of 0.5 min).

This analytical method was validated specifically for these tests and for samples containing between 50 and 100%  $\text{Zn}_3\text{P}_2$ . For samples found to contain less than 50%  $\text{Zn}_3\text{P}_2$ , a linear relationship between analyte concentration and detector response was assumed. (Further work in the DWRC laboratory has indicated that this assumption is valid.) A laboratory in-house reference standard of  $\text{Zn}_3\text{P}_2$  was obtained from H.R. Harkins, Inc. (Pleasant Valley, NY), and certified versus a primary reference standard obtained from the US Environmental Protection Agency. Sample concentrations were calculated versus the in-house reference standard.

## RESULTS

Although great variation existed in the weight of packets sold by different distributors, ranging from 0.16 to 10.45 g, considerable consistency was found in the weights of packets purchased from the same distributors. The

physical properties of the samples varied greatly. Visual differences were evident in color (ranging from a light gray to black) as well as texture from samples purchased from both the same and different distributors. Although most samples were black, irrespective of their purity, all gray samples tested very low in  $\text{Zn}_3\text{P}_2$  content, between 1.4 and 13.8%.

There were no significant differences between samples analyzed from the same packets, confirming the accuracy of the method (sample DFN;  $\bar{x} = 60.2 \pm 1.7$  and  $61.1 \pm 0.9$ ;  $p > 0.05$ ). Analysis of samples from packets obtained from the same distributor indicated fairly uniform purity. However, large variations existed in the purity of samples among the distributors, ranging from nondetectable amounts to 92% (Table 1). Twenty-one of the 23 brands collected tested well below 80%, 14 tested below 15%, and 4 of the brands contained no detectable amounts of

TABLE 1

Analysis of Zinc Phosphide (% Technical Purity) Purchased from Distributors in Bangladesh Between 1988 and 1989 ( $n = 5$ , Unless Otherwise Indicated)

| Sample |                   |              |                                | $\bar{x}\%$ ( $\pm 1$ S.E.) sample |                        |                         |
|--------|-------------------|--------------|--------------------------------|------------------------------------|------------------------|-------------------------|
| ID     | Purchase location | Color        | Wt<br>( $\bar{x}g \pm 1$ S.E.) | June 88                            | July 89                | July 89                 |
| DAL    | Dhaka             | 5            | $0.35 \pm 0.03$                | $55.0 \pm 2.4^a$                   | $37.4 \pm 0.8^b$       |                         |
| DAR    | Dhaka             | 5            | $0.28 \pm 0.05$                | $3.0 \pm 3.0$                      |                        |                         |
| DF     | Dhaka             | 4            | $0.44 \pm 0.10$                | $11.6 \pm 3.0^a$                   | $21.8 \pm 2.5^b$       |                         |
| DM     | Dhaka             | 4            | $3.93 \pm 0.41$                | $14.0 \pm 0.3$                     |                        |                         |
| DJ     | Dhaka             | 3            | $0.98 \pm 0.22$                | $1.4 \pm 0.4$                      |                        |                         |
| DS1    | Dhaka             | 2            | $8.12 \pm 0.00$                | $5.0 \pm 0.0^{n=1}$                |                        |                         |
| DFR    | Dhaka             | 3            | $2.00 \pm 0.11$                | $13.8 \pm 0.7$                     |                        |                         |
| DMS    | Dhaka             | 3            | $3.47 \pm 0.34$                | $12.4 \pm 0.8$                     |                        |                         |
| MMR    | Mirzapur          | 1            | $6.29 \pm 0.24$                | $3.0 \pm 0.0$                      |                        |                         |
| DS2    | Dhaka             | 2            | $9.48 \pm 0.37$                | $4.8 \pm 0.2^{n=4}$                |                        |                         |
| DFN    | Dhaka             | 5            | $0.23 \pm 0.03$                | $60.2 \pm 1.7^a$                   | $30.4 \pm 1.8^b$       |                         |
| DEY    | Dhaka             | 5            | $0.31 \pm 0.02$                | $78.0 \pm 1.0$                     |                        |                         |
| CS     | Comilla           | 5            | $0.27 \pm 0.04$                | $92.1 \pm 1.5^a$                   | $79.2 \pm 1.0^b$       |                         |
| CH     | Comilla           | 5            | $0.24 \pm 0.02$                | $27.8 \pm 0.7$                     |                        |                         |
| CR     | Comilla           | 2            | $0.55 \pm 0.10$                | $7.0 \pm 0.0$                      |                        |                         |
| CJ     | Comilla           | 5            | $0.23 \pm 0.05$                | Not detected <sup>a</sup>          | $47.6 \pm 0.8^b$       |                         |
| CSA    | Comilla           | 5            | $0.27 \pm 0.02$                | $32.6 \pm 4.3^a$                   | $30.0 \pm 0.6^a$       | $14.0 \pm 0.0^{n=4, b}$ |
| CO     | Comilla           | 5            | $0.06 \pm 0.01$                | Not detected <sup>a</sup>          | $36.0 \pm 2.1^b$       |                         |
| CM     | Comilla           | 5            | $0.44 \pm 0.11$                | Not detected <sup>n=2</sup>        |                        |                         |
| CF     | Comilla           | Not recorded | $0.57 \pm 0.03$                | $3.6 \pm 0.6^a$                    | $2.0 \pm 0.0^b$        |                         |
| CK1    | Comilla           | 5            | $0.10 \pm 0.01$                | $49.6 \pm 0.9^a$                   | $2.8 \pm 0.3^{n=4, b}$ | $3.0 \pm 0.0^{n=1, b}$  |
| CK2    | Comilla           | 5            | $0.28 \pm 0.04$                | $35.6 \pm 6.0$                     |                        |                         |
| CA     | Comilla           | 5            | $0.21 \pm 0.02$                | Not detected                       |                        |                         |

Color scale: 5 = black, 4 = light black, 3 = dark gray, 2 = gray, 1 = light gray.

$\text{Zn}_3\text{P}_2$ . Of the 10 brands that were repurchased from the same distributors after 5 or 6 months, the purity of 7 was significantly different ( $p < 0.05$ ;  $t$ -test) from earlier purchased samples.

## DISCUSSION

Zinc phosphide has been and continues to be an important rodenticide in Bangladesh as well as in many other countries of the world for field and urban rodent control. In Bangladesh, Karim (1989) demonstrated that 2%  $\text{Zn}_3\text{P}_2$  baits placed in burrows effectively reduced rodent activity between 68 and 71% during different rice growing stages. When used once a year when rodent populations are low, it is considered cost-effective and environmentally safe (Sultana & Jaeger, 1992), but lack of quality control distorts its use. From the farmers' standpoint, concern is over the amount of  $\text{Zn}_3\text{P}_2$  in each packet. It is clear that much variation has existed in the quality of  $\text{Zn}_3\text{P}_2$  available to farmers for rodent control in Bangladesh, and there seems to have been little consistency in the quality of material sold by the same distributor over time. The material has been sold in a wide range of package weights and by a large number of companies and/or individuals. While much of the material sold was black, packets of gray, brown, and gray with brown specks were also found. One sample that was analyzed looked like soil. Each packet costs between 0.50 and 3.0 taka (about 1 and 8 cents, US).

Distributors in Bangladesh expressed considerable concern over  $\text{Zn}_3\text{P}_2$  deterioration during shelf storage. Although a number of studies have been conducted on the weatherability of baits, very little information actually seems to exist on the stability of the  $\text{Zn}_3\text{P}_2$  powder during shelf storage in containers under either dry or humid conditions. Guerrant & Miles (1969) reported analyzing a sample that had been labeled 94% and stored in a cardboard box for over 13 years as 86.8%, and Elmore & Roth (1943) further reported that it remained unchanged after 180 days on stored grain baits. Lund (1988) further stated that it was stable for several years under normal storage conditions. Anonymous (1967) indicated that the shelf-life of technical material is about 3 years if it is kept dry in tightly closed containers. Because  $\text{Zn}_3\text{P}_2$  powder is stored in paper sacks inside of paper envelopes, some loss of purity would be expected during shelf storage under the humid conditions in Bangladesh, but it would seem to be unlikely that time of shelf storage (which is unknown) would account for such universally low purities in the material sold by so many distributors. The variability found among samples from the same distributor during the time of this study may, however, have been related to shelf time.

During field use,  $\text{Zn}_3\text{P}_2$  is more stable under dry than moist conditions (Hilton & Robinson, 1972; Hayne, 1951). Guerrant & Miles (1969) also reported that when used on apple or potato baits, 70% of the activity remained after 99 days. Hood (1972) reported that baits used in humid sugarcane fields became moldy and disintegrated after 3 weeks, while Gratz (1973) stated that baits exposed in the field deteriorated within 2–3 days, unless prepared with mineral oil. Koehler *et al.* (next article) reported that pelletized baits retained nearly all of their  $\text{Zn}_3\text{P}_2$  concentration during a 16-day exposure to the humid/wet conditions of Hawaii. Storage stability tests are needed under conditions in Bangladesh to determine whether similar deterioration is evident for both technical material and baits; distributors in Bangladesh are reluctant to sell these materials following shelf storage under the often humid, tropical conditions.

In producing bait cakes for controlling rodents, the correct concentration of the active ingredient is very important. If it is too high, rodents will avoid the baits; if it is too low, rodents will ingest sublethal doses, leading to bait shyness. If the percent of active ingredient in the  $\text{Zn}_3\text{P}_2$  purchased by farmers from distributors to make baits or used by formulators to make and sell ready-made baits is less than 80%, the baits will certainly be less effective.

The acute oral  $\text{LD}_{50}$  toxicity of  $\text{Zn}_3\text{P}_2$  to *B. bengalensis*, which weighs about 333 g, has been established at about  $25 \text{ mg kg}^{-1}$  (Htun & Brooks, 1979; Poché *et al.*, 1980; Srihari *et al.*, 1979). Most farmers buying  $\text{Zn}_3\text{P}_2$  packets at local markets or stores have no idea of the quality of the material they are purchasing, nor do they understand the importance of proper formulation. Labels on packets purchased by farmers almost never indicate the purity of the material. If a farmer does not know the actual concentration, and he mixes baits or treats grains assuming 80% a.i.  $\text{Zn}_3\text{P}_2$  technical material, 2% concentrate baits would contain about 16 mg of  $\text{Zn}_3\text{P}_2$  in each gram of bait — twice the  $\text{LD}_{50}$  dose. However, if the  $\text{Zn}_3\text{P}_2$  purchased were actually only 50%, or even 15% as in many of the samples analyzed, the baits would contain 10 and 3 mg, respectively, in each gram of prepared bait. Based on an overnight consumption of about 1.9–3.5 g of 2%  $\text{Zn}_3\text{P}_2$  when given free choice, most rats would be expected to die, as death normally occurs within 24 h following the intake of high doses (Lund, 1988). However, with only 15 or 50% a.i., a rat would need to eat about 12.6 and 3.8 g of bait cakes, respectively, to reach the point of death. At either concentration, few rats would die from exposure to  $\text{Zn}_3\text{P}_2$ , since poisoning symptoms normally are exhibited within 25 min of intake of high doses (Lund, 1988), at which time the rat would quit feeding.

It has been reported (Marko *et al.*, 1989) that there is only one

authorized importer of  $\text{Zn}_3\text{P}_2$  in Bangladesh. M/S Agrani Traders (Mautail, Mrida Bari, Dhaka) has in the past imported 80% a.i.  $\text{Zn}_3\text{P}_2$  from United Phosphorous, Ltd, Bombay, India, for 205 taka for 500 g (about \$4.25 US) and then provided it to five distributors who, in turn, sold it to a large number of companies (many of which apparently are unauthorized to sell the material) within Bangladesh. Whether, as was suggested by these distributors,  $\text{Zn}_3\text{P}_2$  of poor quality was illegally imported into Bangladesh (Marko *et al.*, 1989) or if, in fact, quality material was being adulterated after it was distributed is unknown by us. Soil and charcoal, in some cases, may also be packed and sold as  $\text{Zn}_3\text{P}_2$ . In any case, farmers are aware of the ineffectiveness of much of the available material and no longer want to use it. Zinc phosphide bait cakes were, however, readily accepted by farmers in 1983 and 1984 when it was obvious that the international donor projects had provided them to the farmers. However, in 1990, the Ministry of Agriculture/Directorate of Agricultural Extension, which regulates pesticide use, restricted the sale of  $\text{Zn}_3\text{P}_2$  to the extent that it could only be sold as a formulated bait. But, because retailers are not interested in formulating the baits due to their perception that  $\text{Zn}_3\text{P}_2$  rapidly decomposes, ready-made bait cakes are not available.

To our knowledge, no similar analytical studies have been completed on commercially available  $\text{Zn}_3\text{P}_2$  from other countries in the region, but one would not expect the situation to be entirely unique to Bangladesh. There is currently no product control process within Bangladesh to monitor the quality of  $\text{Zn}_3\text{P}_2$ ; however, it has been recognized that such a program is greatly needed (Marko *et al.*, 1989). Although it would require additional laboratory and enforcement personnel, it could be set up within the government as a regulatory procedure. Alternatively, private groups or associations (with technical and managerial support from nongovernment organizations) might be able to formulate, market, and guarantee quality under a certified trademark (Marko *et al.*, 1989). In any case, some method to assure rodenticide quality is needed if the rodent control technology that is being taught by extension personnel and implemented by farmers is to be effective.

## ACKNOWLEDGEMENTS

This study was conducted with funds provided to the USDA/APHIS/ADC Denver Wildlife Research Center and the Bangladesh Agricultural Research Institute by the US Agency for International Development under Agricultural Research Project II, Vertebrate Pest Management Component of PASA ANE-0051-P-AG-8025-00. We wish to acknowledge

the DWRC Research Support Section for conducting all technical assays of the zinc phosphide and assisting in statistical analysis. Dr Ishwar Prakash confirmed that a similar problem is likely to exist with zinc phosphide in India, but that no studies such as this one have been conducted to verify the situation. We also thank J. E. Brooks, M. W. Fall, and M. M. Jaeger for reviewing and Marilyn Harris for editing drafts of the manuscript.

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